Glycerol acetylation over dodecatungstophosphoric acid immobilized into a silica matrix as catalyst

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ARTICLE INFO

ABSTRACT

The esterification of glycerol with acetic acid was carried out over dodecatungstophosphoric acid (PW) immobilized into a silica matrix. The products of glycerol acetylation were monoacetin, diacetin and triacetin. The immobilization of PW into silica was carried out by two different techniques: sol–gel and impregnation methods. The catalysts prepared by sol–gel method will be denoted as PW-in-S while the catalysts prepared by impregnation will be denoted as PW-on-S. The catalysts were characterized by nitrogen adsorption at 77 K, FTIR, XDR and ICP-AES. A series of PW immobilized into silica with different PW loading were prepared. It was observed that the catalytic activity increases with the amount of PW immobilized into silica, either by the sol–gel method or by the impregnation method.

High values of selectivity to diacetin were obtained with all catalyst.

The effect of various parameters, such as, reaction temperature, catalyst loading, molar ratio of glycerol to acetic acid and reusability of PW-in-S2 were studied to optimize the reaction conditions.

The catalytic stability of the PW-in-S2 was evaluated by performing consecutives batch runs with the same catalyst sample. It was observed a stabilization of the catalytic activity.

1. Introduction

Glycerol is the by-product of the biodiesel production by transesterification of triglycerides with methanol or ethanol. Due to the increase of biodiesel demanding, an increase of glycerol production and a price decline have been observed, becoming the glycerol an attractive molecule for the synthesis of other value chemical products [1,2].

The preparation of the esters of glycerol by esterification with acetic acid is one of the possibilities of glycerol utilization. The products of glycerol acetylation are monoacetin, diacetin and triacetin (Scheme 1). The monoacetin and diacetin have applications in cryogenics and as raw material for the production of biodegradable polyesters [3] while the triacetin has applications going from cosmetics to fuel additive [4–6].

Traditionally, the esterification of glycerol with acetic acid is carried out over mineral acids as catalysts. However, the effluent disposal leads to environmental problems and economical inconveniences. These problems can be overcome by the use of heterogeneous catalysts. Zeolites, amberlyst and niobic acid [7],

mesoporous silica with sulfonic acid groups [8] and Starbon® [9] have been used as solid catalyst in the esterification of glycerol with acetic acid.

Heteropolyacids (HPAs) are typical strong Brönsted acids, which catalyze a wide variety of reactions. The major disadvantages of HPAs as catalysts are their low thermal stability, low surface area (1–10 m^2/g), separation problem from reaction mixtures and solubility [10–14]. A variety of supports like, zeolite [15–19], activated carbon [20–24], silica [25–41], magnesia [42,43], aluminas [44,45] and polymers [46–51] have been used as support to immobilize HPAs, in order to increase the specific area of them or even to increase the number of accessible acid sites of the HPAs.

Industrially, the HPAs have been used as catalysts in the oxidation of methacrolein to methacrylic acid, oxidation of ethylene to acetic acid and hydration of olefins [14].
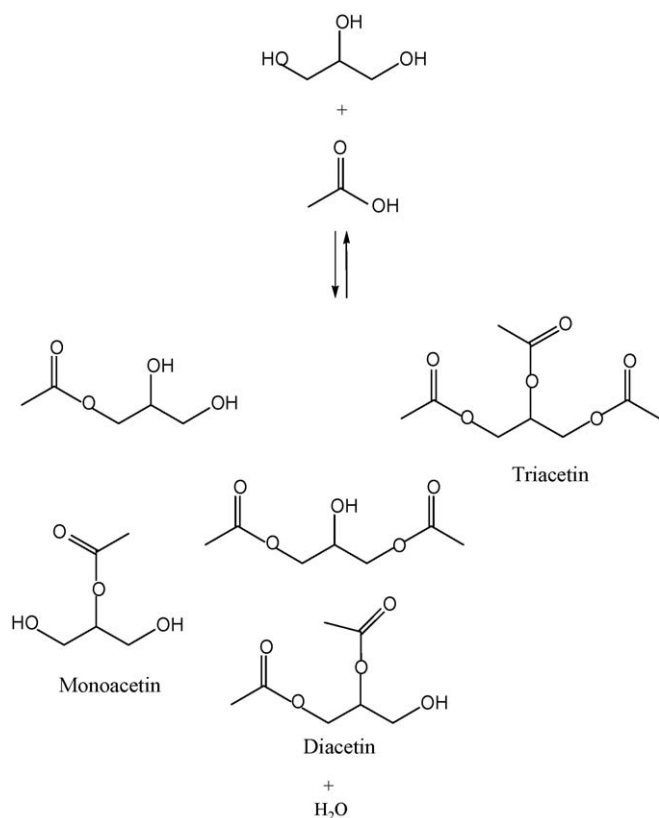
In a previous work [52], dodecamolybdophosphoric acid encaged in the USY zeolite was used as catalysts in the esterification of glycerol with acetic acid. It was observed that the catalytic activity increases with the amount of heteropolyacid immobilized in the USY. However, at high amount of the dodecamolybdophosphoric acid encaged in the USY zeolite, a decrease of the catalytic activity was observed.

In this work, we study the esterification of glycerol with acetic acid over dodecatungstophosphoric acid (H$_3$PW$_{12}$O$_{40}$) immobilized into silica matrix. The influence of various reaction

Scheme 1. Schematic representation of the glycerol acetylation.

parameters such as temperature, molar ratio of acetic acid to glycerol and catalyst loading on the activity is also studied.

2. Experimental

2.1. Preparation of the catalysts

The immobilization of PW into silica matrix was carried out by two different techniques: sol–gel and impregnation methods.

2.1.1. PW-in-silica
The catalysts samples were prepared according to Izumi et al. [30], by the sol–gel technique. A mixture of water (2.0 mol), 1-butanol (0.2 mol) and heteropolyacid (PW) (5.0×10^{-4} mol) was added to tetraethyl orthosilicate (0.2 mol) and stirred at 80 °C during 3 h. The hydrogel obtained was dehydrated slowly at 80 °C for 1.5 h in vacuo (25 Torr). The dried gel obtained was extracted in a sohxlet apparatus with methanol during 72 h, and dried at 100 °C, overnight. The silica-included heteropolyacid was dried at 100 °C for 3 h prior to use in the catalytic reactions. The sample catalysts will be denoted as PW-in-S.

2.1.2. PW-on-silica
The PW supported on silica were prepared by impregnation method according Pizzio et al. [31]. Briefly, 1 g of silica gel (Aerosil 200, Degussa) was impregnated with 4 cm³ of PW solution, using ethanol/water (1:1, v/v) as solvent, under constant stirring for 72 h. The slurry was evaporated to dryness, followed by calcination at 170 °C, during 4 h. The sample catalysts will be denoted as PW-on-S.

2.2. Characterization of the catalysts

The textural characterization of the catalysts was based on the nitrogen adsorption isotherm, determined at 77 K with a Micromeritics ASAP 2010 apparatus.

The X-ray diffraction (XRD) patterns of the heteropolyacid, silica and catalysts were obtained by using a Bruker powder diffractometer with built-in recorder, using Cu Kα radiation, nickel filter, 30 mA and 40 kV in the high voltage source, and scanning angle between 5° and 55° of 2θ at a scanning rate of 1°/min.

FTIR spectra were record on a Bio-Rad FTS 155 FTIR spectrometer at room temperature in KBr pellets over range of 400–4000 cm^{-1} under atmospheric conditions.

The amount of dodecatungstophosphoric acid immobilized into silica matrix was measured by dissolving the catalyst in H_2SO_4/HF 1:1 (v/v) and analyzing the obtained solution using inductively coupled plasma analysis (ICP), which was carried out in a Jobin-Yvon ULTIMA instrument.

Catalyst acidity was measured by potentiometric titration, according Pizzio et al. [31]. A small quantity of n-butylamine solution (0.05 N) in acetonitrile was added to a known mass (0.05 g) of solid suspended in acetonitrile (90 mL), and shaken for 3 h. Then, the suspension was potentiometrically titrated with the same solution of n-butylamine in acetonitrile. The electrode potential variation was measured with a Crison micropH 2001 instrument.

Scanning electron microscopy (SEM) of the catalysts was carried out using a Hitachi model S-2400.

2.3. Catalytic experiments

The catalytic experiments were carried out in a stirred batch reactor at reflux conditions. In a typical experiment, the reactor was loaded with 20 mL (0.350 mol) of acetic acid, 2 g (0.022 mol) of glycerol and 0.2 g of catalyst. In all experiments, the stirrer speed was kept constant at 500 rpm. Under this reaction conditions, a good miscibility of glycerol in acetic acid was observed.

The stability tests of the PW-in-S2 and PW-on-S3 were carried out by four consecutive experiments, at the same reaction conditions. Between the catalytic experiments, the catalyst was separated from the reaction mixture by centrifugation, washed with water and dried at 120 °C overnight.

Samples were taken periodically and analysed by GC, using a KONIC HRGC-3000C instrument equipped with a 30 m × 0.25 mm DB-1 column. Analyses were carried out according to the following temperature program: initially, the oven temperature was at 60 °C. The temperature increased from 60 °C to 250 °C, with a slope of 10 °C/min^{-1}. The temperature of injector is 250 °C, while the detector temperature is 300 °C. The products mono-, di- and triacetin were identified and their response factor were determined with respect to the starting material from GC analysis using known compounds in calibration mixtures of specified composition.

3. Results and discussion

3.1. Catalysts characterization

The nitrogen adsorption–desorption isotherms of the silica support and the PW-silica catalysts are shown in Fig. 1. It was observed that the introduction of HPA on silica by the sol–gel method (PW-in-S1 and PW-in-S2) created a microporous material. Similar results were also observed by Izumi et al. [30].

Table 1 shows the textural characterization of the catalysts. The specific surface area (S_{BET}) was determined using the BET method while microporous volume (V_{micro}) and external surface area (S_{ext}) were determined by the t-method, using a standard isotherm proposed by Greeg et al. [53]. For the PW-in-S catalysts series, which were prepared by the sol–gel method, it was observed that immobilization of HPAs in silica created a microporous material. A similar result was also reported by Izumi et al. [30]. A continuous decrease of the microporous volume and the surface area with the
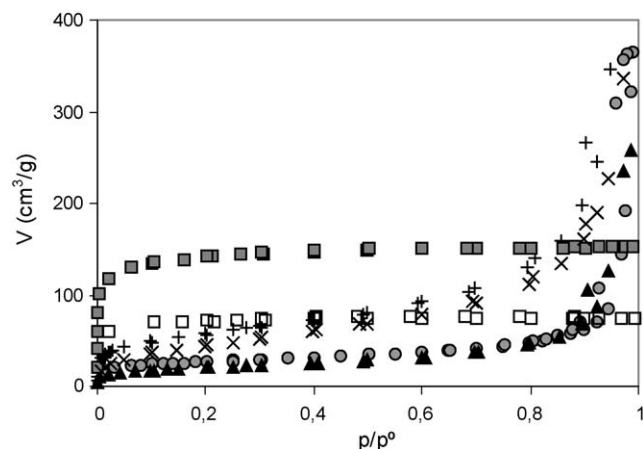
Fig. 1. N_2 adsorption–desorption isotherm of the catalysts. (+) Silica; (×) PW-on-S1; (⬤) PW-on-S2; (▲) PW-on-S3; (▣) PW-in-S1; (□) PW-in-S2.

Table 1
Physicochemical characterisation of catalyst sample.

Sample	Amount HPA[a] ($g_{HPA}/g_{support}$)	Surface area[b] (m^2/g)	External Surface area[c] (m^2/g)	Microporous volume[c] (cm^3/g)
Silica	–	223	217	0.018
PW-in-S1	0.025	489	4.1	0.230
PW-in-S2	0.065	254	1.5	0.114
PW-on-S1	0.012	204	193	0.004
PW-on-S2	0.098	93	59	0.003
PW-on-S3	0.155	70	65	0.002

[a] ICP.
[b] BET.
[c] t-Method.

amount of PW immobilized into a silica matrix was also observed. The reduction in the surface area and the microporous volume of the catalysts may be due to the blockage of the pores by active species. A similar result was also observed by Rafiee et al. [40]. For the PW-on-S catalysts series, a reduction of the surface area (S_{BET}), external surface area (S_{ext}) and microporous volume with the amount of PW immobilized on silica support was observed. The PW-in-S catalysts exhibit higher surface areas than the PW-on-S catalyst (Table 1).

Fig. 2 shows the FTIR spectra of the PW (Fig. 2A), silica (Fig. 2B), PW-in-S1 (Fig. 2C), PW-in-S2 (Fig. 2D), PW-on-S1 (Fig. 2E), PW-on-S2 (Fig. 2F) and PW-on-S3 (Fig. 2G). Pure PW exhibited typically three major IR bands located at 1080, 985 and 890 cm^{-1} attributed to absorption modes of Keggin ion $[PW_{12}O_{40}]^{3-}$. The bands at 1080, 985 and 890 cm^{-1} are assigned as to the stretching modes of
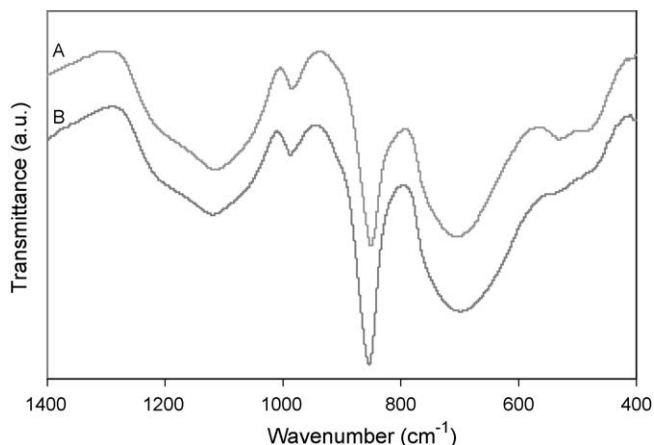

Fig. 3. FTIR spectra: differential spectrum of (A) PW-in-S1; (B) PW-in-S2.

oxygen atom bond to tungsten and phosphorous, W=O, P–O and W–O–W edge, respectively [31,54]. The spectrum of catalysts prepared by impregnation method (PW-on-S) shows the peaks typical of the Keggin structures of PW. In all catalysts, it should be noted that the heteropolyacid bands placed between 1000 and 1100 cm^{-1} is masked with the silica band. However, it was observed that some peaks typical of the Keggin structures of PW are overlapped or partially overlapped with the peaks of silica matrix framework, in the spectrum of the catalysts prepared by sol–gel method (PW-in-S). The differential spectrum of PW-in-S1 (Fig. 3A) and PW-in-S2 (Fig. 3B) shows the presence of typical peaks characteristic of Keggin structures. These results suggest that the PW immobilized on silica by sol–gel method keep the Keggin structure.

XRD patterns of the PW, silica, PW-in-S and PW-on-S catalysts are shown in the Fig. 4. The XRD diffractograms of the PW-in-S and PW-on-S catalysts do not indicate the presence of any crystalline phases related to PW indicating that the particles are too small or well dispersed to be detected by XRD. It is only observed a broad band centered around $2\theta = 25°$ (amorphous silica). A similar phenomenon was also observed by Molnár et al. [41].

Fig. 5 shows the SEM of the silica (Fig. 5A) and PW-in-S2 catalyst (Fig. 5B). It is observed that the immobilization of the heteropolyacid in the silica by sol–gel method leads to a heterogeneous particle size distribution. Similar results were also observed by Chimienti et al. [25].

Fig. 6 shows the curves obtained by means of potentiometric titration with n-butylamine. The initial electrode potential (Ei) indicates the maximum acid strength of the surface sites [31]. The
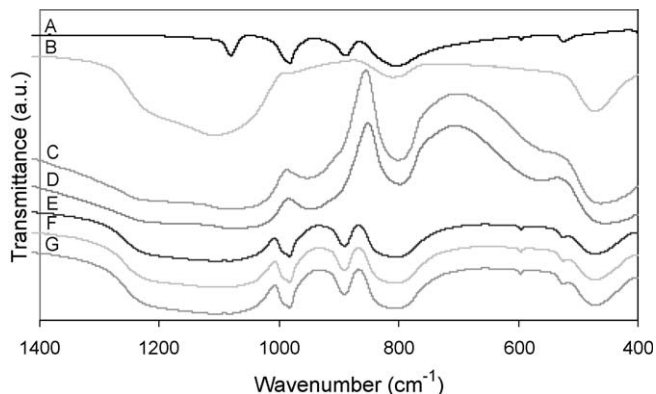

Fig. 2. FTIR spectra: (A) PW; (B) silica; (C) PW-in-S1; (D) PW-in-S2; (E) PW-on-S1; (F) PW-on-S2; (G) PW-on-S3.
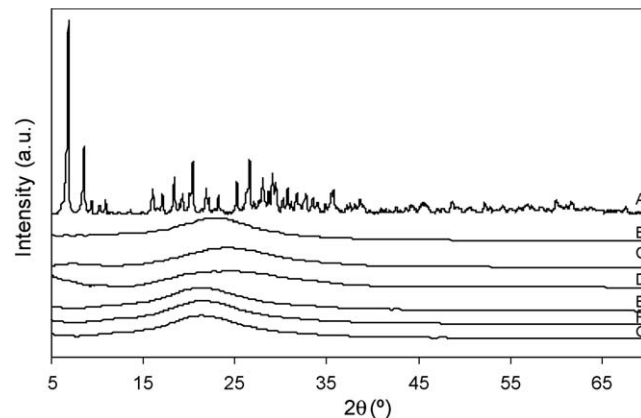

Fig. 4. XRD patterns of (A) PW; (B) silica; (C) PW-in-S1; (D) PW-in-S2; (E) PW-on-S1; (F) PW-on-S2; (G) PW-on-S3.
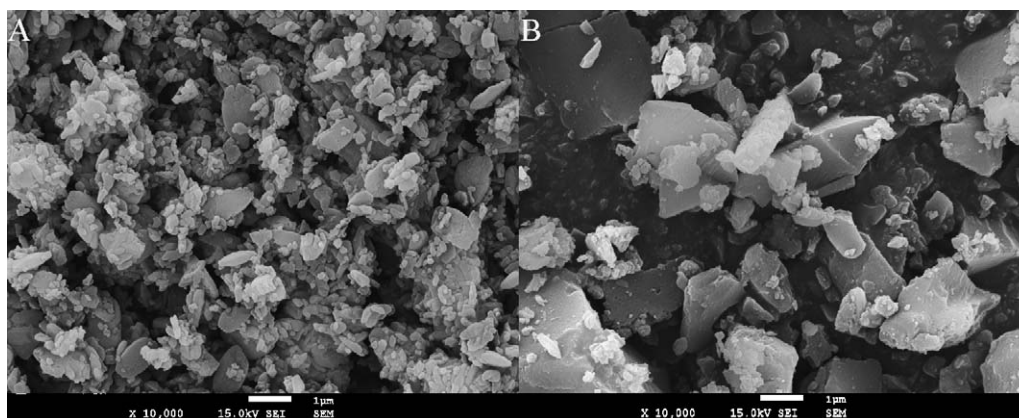
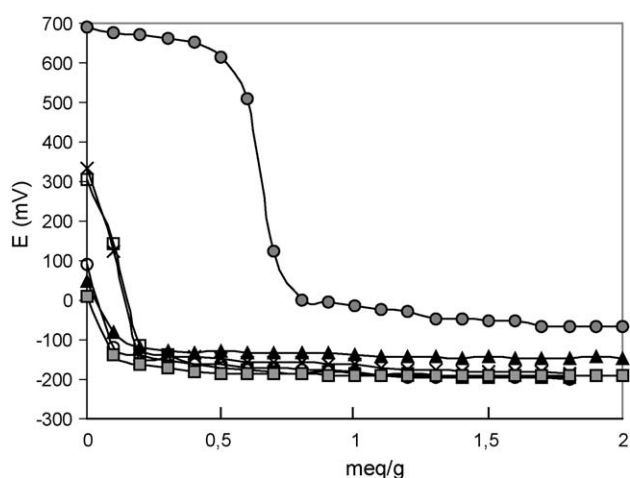**Fig. 5.** Scanning electron micrograph of (A) silica; (B) PW-*in*-S2.

Fig. 6. Potentiometric titration with *n*-butylamine of the catalysts. (■) Silica; (○) PW-*in*-S1; (□) PW-*in*-S2; (▲) PW-*on*-S1; (×) PW-*on*-S2; (●) PW-*on*-S3.
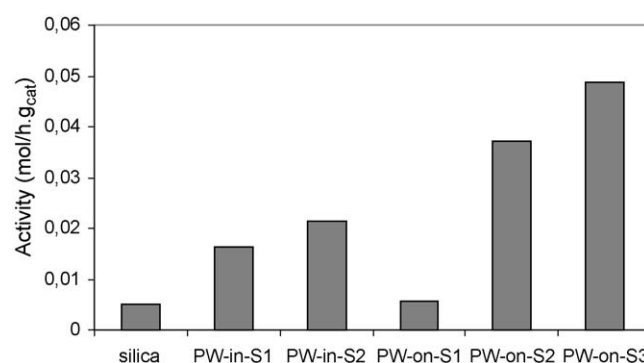

Fig. 7. Esterification of glycerol with acetic acid over PW immobilized into silica matrix. Initial activities taken as the maximum observed reaction rate. Reaction conditions: molar ratio of glycerol to acetic acid = 1:16; Temperature = 120 °C; catalyst loading =0.2 g.

acidic strength of surface sites can be assigned according to the following ranges: very strong site, Ei > 100 mV; strong site, 0 < Ei < 100 mV; weak site, −100 < Ei < 0 mV and very weak site, Ei < −100 mV [31]. Table 2 shows the maximum strength of the catalysts. It is observed that the PW-*on*-S3 sample shows the highest maximum strength. It is also observed that the acidic strength of the catalysts increases with the amount of hetero-polyacid immobilized into silica matrix (Table 1).

3.2. Catalytic experiments

The acetylation products of glycerol over dodecatungstopho-sphoric acid immobilized into a silica matrix were monoacetin, diacetin and triacetin (Scheme 1).

The Fig. 7 compares the initial activity of PW-*in*-S and PW-*on*-S catalyst loaded with different HPA amounts on the esterification of glycerol with acetic acid. The initial catalytic activity was

calculated from the maximum slope of the experimental kinetic curve of glycerol divided by the catalyst (PW plus support) amount. For the PW-*in*-S catalysts, it was observed that the initial catalytic activity increases with the amount of HPA immobilized in silica (PW-*in*-S1 and PW-*in*-S2). This behaviour can be explained due to the increases of the acid strength of the catalysts (Table 2). The PW-*on*-S catalysts showed to have a similar behaviour in comparison to the PW-*in*-S catalysts for the esterification of glycerol with acetic acid (Fig. 7). It was observed that the catalytic activity increases with the amount of PW immobilized on silica support (Table 1).

Table 3 shows the glycerol conversion and the selectivity to the products obtained by the esterification of glycerol with acetic acid over PW immobilized into a silica matrix, after 7 h of the reaction. It can be seen that the sample PW-*in*-S2 exhibits the highest conversion. After 7 h of reaction, the glycerol conversion was 87%,

Table 2
Potentiometric titration results of the catalyst sample.

Sample	Maximum acid strength (mV)
Silica	8
PW-*in*-S1	90
PW-*in*-S2	303
PW-*on*-S1	47
PW-*on*-S2	332
PW-*on*-S3	689

Table 3
Conversion and selectivity to the products of the esterification of glycerol with acetic acid over PW immobilized into a silica matrix. Reaction conditions: molar ratio of glycerol to acetic acid = 1:16; Temperature = 120 °C; catalyst loading = 0.2 g.

Sample	Conversion[a]	Selectivity (%)			
	(%)	Monoacetin	Diacetin	Triacetin	Others
Silica	15	59	25	1	15
PW-*in*-S1	70	25	65	8	2
PW-*in*-S2	87	36	59	4	1
PW-*on*-S1	62	55	34	2	9
PW-*on*-S2	77	28	66	4	2
PW-*on*-S3	82	30	64	5	1

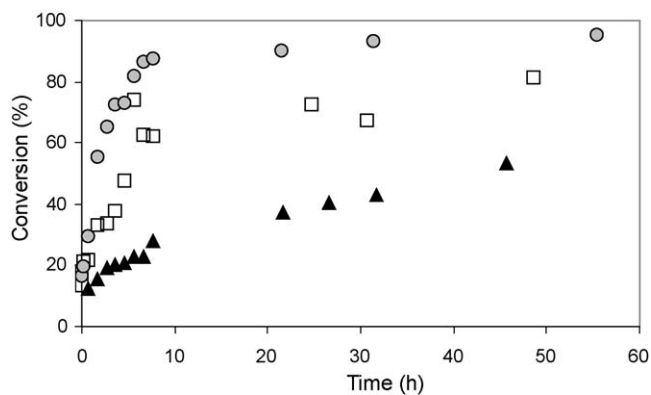[a] Glycerol conversion after 7 h of reaction.

Fig. 8. Esterification of glycerol with acetic acid over PW-*in*-S2 catalyst. Effect of temperature. Conversion (%) *versus* time (h): (●) $T = 120\ °C$; (□) $T = 90\ °C$; (▲) $T = 60\ °C$. Reaction conditions: molar ratio of glycerol to acetic acid = 1:16; catalyst loading = 0.2 g.

Fig. 9. Esterification of glycerol with acetic acid over PW-*in*-S2 catalyst. Effect of catalyst loading. Conversion (%) *versus* time (h): (▲) $m = 0.10$ g; (●) $m = 0.20$ g; (□) $m = 0.30$ g. Reaction conditions: molar ratio of glycerol to acetic acid = 1:16; Temperature = 120 °C.

with a selectivity of 59% to diacetin, 36% to monoacetin and 4% to triacetin. The high selectivity to diacetin can be explained due to the diacetin and the triacetin products to be formed through consecutive esterification reactions.

In order to check the reproducibility and obtain the standard deviation of the catalyst experiment carried out over PW-*in*-S2 sample, the experiment was repeated three times. The reaction conditions were: molar ratio of glycerol to acetic acid = 1:16, Temperature = 120 °C and catalyst loading = 0.2 g. It was observed that, after 7 h of reaction, the following results: glycerol conversion 87.3% ± 0.6%; selectivity to monoacetin 35.3% ± 1.2%; selectivity to diacetin 60% ± 1.0%; selectivity to triacetin 4.3% ± 0.5%. It can be conclude that the experimental error is acceptable and not excessively significant. Similar results were also observed by Melero et al. [8].

3.2.1. Influence of reaction parameters

3.2.1.1. Reaction temperature. In order to evaluate the influence of reaction temperature on the esterification of glycerol with acetic acid over PW-*in*-S2, different experiments were carried out. The reaction temperature was varied from 60 °C to 120 °C, while the ratio glycerol:acetic acid and the amount of catalysts were kept constant. As expected, the conversion increased with the temperature (Fig. 8). The effect of temperature on glycerol conversion and on the selectivity to the reaction products is shown on the Table 4. It was observed that when the esterification of glycerol with acetic acid is carried out at 120 °C, after 7 h, the selectivity to diacetin is 59 at 87% of glycerol conversion.

3.2.1.2. Catalyst loading. Fig. 9 shows the effect of catalyst loading (PW-*in*-S2) on the glycerol conversion. The ratio of glycerol:acetic acid and the temperature were kept constant. The increase of catalyst loading from 0.1 g to 0.2 g showed substantial effect on the glycerol conversion. However, when the catalyst amount increases
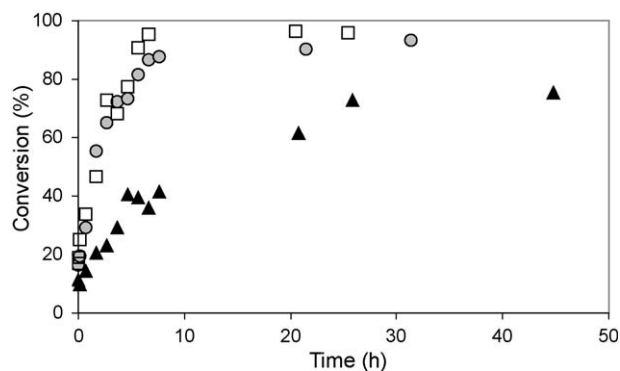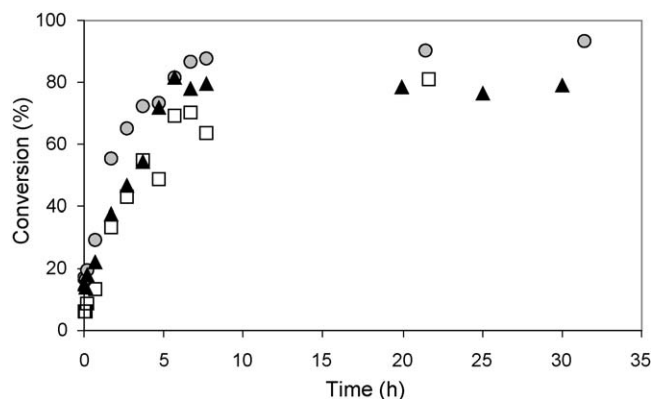

Fig. 10. Esterification of glycerol with acetic acid over PW-*in*-S2 catalyst. Effect of molar ratio of glycerol to acetic acid. Conversion (%) *versus* time (h): (□) 1:6; (▲) 1:11; (●) 1:16. Reaction conditions: Temperature = 120 °C; catalyst loading = 0.2 g.

from 0.2 g to 0.3 g, only a slight increase on glycerol conversion was observed. Thus, it is clear that the increase in catalyst loading above 0.2 g did not help to improve the initial rate of the reaction. This behaviour can be explained due to the increase in the total number of available active catalytic sites for the reaction. A similar result was also observed by Teo and Saha [55] on the esterification of acetic acid with isoamylic alcohol over ion-exchange resins.

The Table 5 shows the effect of the catalyst loading in the selectivity of the PW-*in*-S2 to the different product of the esterification of glycerol with acetic acid. It was observed that all catalyst loading gives good selectivity values to diacetin.

3.2.1.3. Molar ratio of glycerol to acetic acid. In order to study the influence of the mixture chemical composition on glycerol conversion, the glycerol/acetic acid ratio was varied using the proportions 1:6, 1:11 and 1:16 at reaction temperature of 120 °C

Table 4
Conversion and selectivity to the products of the esterification of glycerol with acetic acid over PW-*in*-S2 catalyst. Effect of temperature. Reaction conditions: molar ratio of glycerol to acetic acid = 1:16; catalyst loading = 0.2 g.

Temperature	Conversion[a]	Selectivity (%)			
°C	(%)	Monoacetin	Diacetin	Triacetin	Others
60	29	68	15	1	16
90	62	52	43	1	4
120	87	36	59	4	1

[a] Glycerol conversion after 7 h of reaction

Table 5
Conversion and selectivity to the products of the esterification of glycerol with acetic acid over PW-*in*-S2 catalyst. Effect of catalyst loading. Reaction conditions: molar ratio of glycerol to acetic acid = 1:16; Temperature = 120 °C.

Catalyst	Conversion[a]	Selectivity (%)			
loading (g)	(%)	Monoacetin	Diacetin	Triacetin	Others
m = 0.10	42	27	66	5	2
m = 0.20	87	36	59	4	1
m = 0.30	99	24	70	5	1

[a] Glycerol conversion after 7 h of reaction.

Table 6
Conversion and selectivity to the products of the esterification of glycerol with acetic acid over PW-*in*-S2 catalyst. Effect of molar ratio of glycerol to acetic acid. Reaction conditions: Temperature = 120 °C; catalyst loading = 0.2 g.

Ratio of glycerol: acetic acid	Conversion[a] (%) 4 h (7 h)	Selectivity (%) 4 h (7 h)			
		Monoacetin	Diacetin	Triacetin	Others
1:6	48 (70)	36 (29)	60 (66)	1 (3)	3 (2)
1:11	49 (79)	30 (23)	63 (70)	3 (5)	4 (2)
1:16	74 (87)	33 (36)	62 (59)	3 (4)	2 (1)

[a] Glycerol conversion after 4 h and 7 h of reaction.
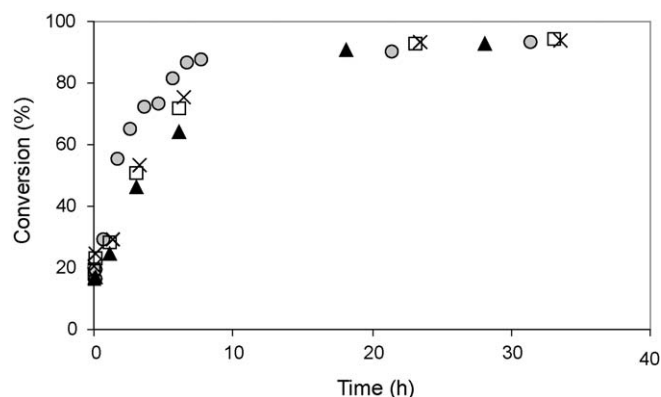

Fig. 11. Esterification of glycerol with acetic acid over PW-*in*-S2 catalyst. Reusability of PW-*in*-S2. (●) 1st use; (□) 2nd use; (▲) 3rd use; (×) 4th use. Reaction conditions: molar ratio of glycerol to acetic acid = 1:16; Temperature = 120 °C; catalyst loading = 0.2 g.

for sample PW-*in*-S2. According to Fig. 10, the glycerol conversion increases with the molar ratio of glycerol to acetic acid. The Table 6 shows the effect of molar ratio of glycerol to acetic acid in the selectivity of the PW-*in*-S2 to the monoacetin, diacetin and triacetin. It was observed that high molar ratio of glycerol to acetic acid leads in lower selectivity values to monoacetin, which can be explained due to the high glycerol conversion promote the diacetin and triacetin formation. According to Melero et al. [8], it is necessary to use high acetic acid excess in order to push the equilibrium toward the simultaneous enhancement of the conversion of glycerol and the selectivity to the most valuable di- and tri-acetylated products. It is also observed that indifferent to the ratio, there is high selectivity to the diacetin (Table 6).

3.2.1.4. Catalysts stability. In order to study the catalytic stability, the PW-*in*-S2 catalyst was reused. Consecutive batch runs with the same catalyst sample and in the same reaction conditions were carried out. Fig. 11 shows the glycerol conversion *versus* time. It is observed a slight decreases of the catalytic activity in the second run. However, similar catalytic activity was observed after the third use.

The PW-*on*-S3 catalyst was also reused. A decrease of the catalytic activity from the first to the forth use was observed (Table 7). This behaviour can be explained due to the leaching of heteropolyacid from the catalysts to the liquid phase.

Table 7
Stability studies of PW-*on*-S3 catalyst on the esterification of glycerol with acetic acid. Reaction conditions: molar ratio of glycerol to acetic acid = 1:16; Temperature = 120 °C; catalyst loading = 0.2 g.

Experiments	Activity × 10² (mol/h g_{cat})
First use	4.87
Second use	3.53
Third use	2.95
Forth use	2.65

4. Conclusions

Dodecatungstophosphoric acid (PW) immobilized into a silica matrix was used in the esterification of glycerol with acetic acid. The products of glycerol acetylation were monoacetin, diacetin and triacetin.

A series of PW immobilized into silica with different PW loading were prepared. It was observed that the catalytic activity increases with the amount of PW immobilized into silica.

High values of selectivity to diacetin were obtained with all catalyst.

In order to study and optimize the reaction conditions, the effect of various parameters, such as, reaction temperature, catalyst loading, molar ratio of glycerol to acetic acid and reusability of PW-*in*-S2 were carried out.

Catalytic stability of the PW-*in*-S2 was evaluated by performing consecutives batch runs with the same catalyst sample. After the second batch, it was observed a stabilization of the catalytic activity.

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